N91-23042

DUAL ION BEAM PROCESSED DIAMONDLIKE FILMS FOR INDUSTRIAL APPLICATIONS

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INTRODUCTION

Diamondlike carbon (DLC) films have generated interest due to the unique properties of the material. The durable, smooth, adherent films are quite transparent and impervious to reagents which dissolve graphitic and polymeric carbon structures. These amorphous films have desirable characteristics similar to those of diamond, such as extreme hardness, high transparency (both at visible and infrared wavelengths), high electrical resistivity, low coefficient of friction, and chemical inertness. They do not, however, have the long range order of the diamond crystal structure. Most importantly, DLC films can be deposited on surfaces at room temperature, allowing a broad range of applications. At NASA Lewis Research Center, single and dual beam ion source systems are used to generate amorphous DLC films, which have been evaluated for a variety of applications including protective coatings on transmitting materials, power electronics as insulated gates and corrosion resistant barriers. A list of the desirable properties of DLC films along with potential applications identified at NASA Lewis and those focused DLC film applications presently being developed at Diamonex, Inc. are presented herein.

DUAL BEAM ION SOURCE SYSTEM AND DLC DEPOSITION PROCEDURE

A 30-cm diameter ion source with its extraction grids masked to 10 cm in diameter is used to directly deposit DLC films. The ion source, developed for electric propulsion technology, uses argon gas in the hollow cathode located in the main discharge chamber, as well as in the neutralizer (ref. 1). After a discharge is established between the cathode and the anode, methane (CH_4) is introduced through a manifold into the discharge chamber. For the depositions presented in this paper the molar ratio of CH_4 to argon was 0.28. This ratio was found to be ideal for generating films at NASA Lewis. In these experiments the total ion beam energy is the sum of the discharge voltage and the screen grid voltage and is around 100 eV. Typically current densities at these conditions are 1 ma/cm^2 at a distance of 2.5 cm axially downstream of the grids (ref. 2). Films are deposited at these conditions on Si and SiO_2 at deposition rates as high as 71 Å/min to film thicknesses as great as 1.5 μm.

It is believed that the amorphous carbon films are produced under conditions where both growth and sputtering occur simultaneously, increased sputtering may decrease the number of graphite precursors incorporated in the films and hence improve film quality.

In addition, Marinow and Dobrew (ref. 3) have found that active sites for nucleation are created, and the growth and coalescence of the nuclei enhanced due to an increased mobility of the condensing atoms when film structures are bombarded by inert gas beams. With these factors in mind, a dual beam system was created by adding an 8-cm diameter argon ion source. This system, shown in figure 1, was used to generate another set of DLC films. The 8-cm source, using a filament cathode, was located at a 12° angle with respect to the 30-cm source and 25 cm from the substrate. There was no observed interaction between the two sources or the ion beams during operation.

The 8-cm ion source was used to direct a beam of energetic argon ions (200 to 600 eV) at a current density of 25 $\mu a/cm^2$ on the substrates while the deposition from the 30-cm ion source was taking place. The beams were approximately monoenergetic, however no mass selection was attempted to determine species.

PROPERTIES OF DIAMONDLIKE FILMS

OPTICAL PROPERTIES OF FILMS

Shown in figure 2 is the spectral transmittance for DLC films generated using the single and dual beam ion source systems. The 1500 Å thick dual beam film has greater transmittance at all wavelengths when compared to the 1500 Å thick single beam films. Some thinner DLC films (800 to 1500 Å thick) look clear to yellowlike in appearance and films thicker than 1500 Å usually look brown. A DLC conformed complete cover coating can usually be obtained for films as thin as 500 Å. The 500 Å thick film presented in figure 2 has transmittance values greater than 90 percent at wavelengths greater than 7000 Å. It is the goal of a joint effort by NASA Lewis and Diamonex, Inc. to obtain clear DLC films, 1000 Å thick, with a transmittance of 85 percent at a wavelength of 5000 Å (the peak of the visible spectrum). Diamonex, Inc. (90 Winsor Drive, Allentown, Pa. 18106) has been in a DLC film technology transfer program with NASA Lewis.

Figure 3 shows the results of some of the on-going studies at NASA Lewis using the dual beam system to reduce the absorption at 5000 Å and hence improve the transmittance. Shown in the figure is the transmittance at 0.5 μm (the peak of the visible) for a DLC film on quartz for various dual beam gaseous deposition conditions. Figure 3 clearly shows that a higher transmittance can be obtained by using the dual beam system where the second ion source uses hydrogen gas. The role of energetic hydrogen in improving transmittance of the DLC film is still under investigation.

The infrared transmittance of DLC films has been shown to be 100 percent transmitting in the wavelength region between 2.5 and 20 μm. DLC films of controlled thickness have been shown to improve the transmittance of Ge infrared optics (refs. 4 and 5). Because the index of refraction (~2) of DLC films is intermediate between Ge and air, a DLC coating is capable of improving overall transmittance by reducing interface reflection losses. A DLC coating can also be used to reduce reflection loses of Si. The high hardness of these films also imparts abrasion protection to these infrared optical materials.

Listed in table I are values of H/C ratio, optical band gap, index of refraction, absorption coefficient and solar transmittance for DLC films generated using the single or dual beam ion sources. Certain properties are enhanced by using a dual beam system, mainly the solar transmittance which is higher, as is the index of refraction, and a lower absorption coefficient, when compared to the single ion source films. The optical band gap and density for the single and dual beam system films are similar. Also listed in table I are values of resistivity, density, and adherence. Since all of the NASA Lewis DLC films were processed in oil diffusion-pumped facilities without the benefit of liquid nitrogen cryo-traps, even higher quality films might be obtained by using a helium cryopumped facility.

CHEMICAL AND PHYSICAL PROPERTIES

The DLC single and dual beam films were subjected to a solution of 3 parts H_2SO_4 and 1 part HNO_3 (concentrated acids, by volume) at 80 °C for periods up to 20 hr. The films on silicon were unaffected by the reagent. These results clearly indicate that the films are far more resistant to chemical etching than normal polymeric hydrocarbons or graphite. Dr. J.C. Angus (ref. 6) measured the diffusion coefficient of Argon, trapped at the DLC film/substrate interface, to be less than 10^{-18} cm^2/sec. This value is 10 orders of magnitude (10 billion) times less than conventional hydrocarbons or polymers. Thus DLC films are one of the best known hermetic barriers. This suggests the potential use of the DLC films as chemical and/or a diffusion barrier for microelectronic or optical components.

Transmission electron microscopy at 30 000 X showed the films to be smooth and essentially free of features. No pinholes or other defects were observed.

The adherence of the films on quarts was measured following the procedure used by Mirtich (ref. 7). The adherence of the films generated with either the single or dual beam systems were as good as the maximum adherence of the Sebastian Adherence Tester© used in the measurement ($\sim 5.5 \times 10^7$ N/m^2 or 8000 psi). The film adherence was extremely high and frequently found to exceed the cohesion of the substrate such that portions of quarts gave way with the film still intact.

Some films deposited with the dual beam on Si have been stored for 10 years and show no visible signs of deterioration. Figure 4 shows a plot of the coefficient of friction for a diamondlike carbon film sliding on steel as a function of relative humidity. For a humidity less than one percent the coefficient of friction is very low, indicating a potential use of a DLC film as a wear resistant surface for inert or vacuum environments.

Scratch tests were performed on DLC films depicted on quarts by rubbing SiO_2 particles ($\sim$80 μm) over the surface. Figure 5 shows the result of these tests. The DLC film protected the quarts from the abrasive effects of the SiO_2 particles.

Table II lists the properties of diamondlike films and compares them to those of natural diamond and polycrystalline diamond films (ref. 8). In a couple of categories DLC films do not quite measure up to those of polycrystalline or natural diamond. For instance, natural diamond and polycrystalline diamond have thermal conductivities of 900 and 700 W/mK respectively; whereas, a DLC film is only 7 W/mK. Likewise, the resistivity of DLC films is not as high as that of diamond. Although the microhardness of DLC films (5 000 kg/mN^2) is approximately half (½) of that of diamond, it is twice as hard as hard corundum (2 085 kg/mN^2) and harder than sapphire. This hardness value makes DLC films a good coating when a hard surface is desirable (i.e., magnetic memory protection, eyeglass lenses, etc.). The coefficient of friction (0.1) for a diamondlike film at low humidity is similar to that of natural diamond. Thus any material that is affected by wear has the potential to benefit from the reduced friction properties and hardness of diamondlike coatings.

The distinguishing difference between DLC film and polycrystalline film is that DLC films are smooth, adherent and are deposited at room temperature or less. This feature of DLC films alone makes them a popular coating choice in a vast area of applications. Whereas, polycrystalline diamond films, which are rough, not very adherent and not specularly transmitting as yet, have the limiting feature of having the substrate at temperatures greater than 600 °C during deposition. This limits polycrystalline diamond film's applications.

POTENTIAL APPLICATIONS

A feasibility study of commercial applications of diamondlike films was done at the NASA Lewis. The objective of the study was to evaluate, rank, recommend and plan commercial applications for NASA-developed diamondlike film deposition technology. The approach was to identify potential users, prioritize potential applications and assess the feasibility of selected applications. A questionnaire was mailed to 230 companies. The number of responses returned was 39 with a total of 44 applications identified. Table III presents the top 12 potential applications identified by the study that appear, at the moment, feasible using diamondlike films. There are, of course, many other applications not listed here but bear mentioning like durable luster enhancing coatings for gemstones, abrasion resistant coatings for plastics, etc.

Shown in table IV are the focused diamondlike film applications at Diamonex, Inc., is a new corporation founded in 1990 whose principle technologies are polycrystalline diamond and diamondlike films. They have purchased an exclusive license to the NASA Lewis dual ion beam patent to make diamondlike films. Diamonex has the rights to also sublicense the patent. Because of some of the properties of DLC films listed in table II, the technical feasibility and the user need, they have focused their resources on making abrasion-resistant optical coatings their number one priority. Other applications listed include the use of DLC films as a hermetic seal of transparent substrates and wear protection of nonoptical substrates.

SUMMARY

A major advantage of DLC films is that they are smooth and adherent and can be deposited on substrates at room temperature. These features allow DLC films to be used readily in many applications where properties of DLC films such as hardness, scratch resistance, hermeticity and transparency are important. Included in this paper are prioritized lists of many potential DLC film applications.

Diamonex, Inc., which has a license to NASA Lewis dual ion beam DLC film patent, has estimated the DLC film potential market to be several billion dollars. The abrasion-resistant optical coatings market for eyeglass lenses alone is estimated at a half a billion dollars. Diamonex is authorized to grant sub-licenses under their exclusive license arrangement from NASA.

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TABLE I - OPTICAL, CHEMICAL AND PHYSICAL PROPERTIES OF DLC FILMS GENERATED USING CH_4 WITH SINGLE OR DUAL BEAM ION SOURCES

	Single beam CH_4/A = 28 percent	Dual beam CH_4/A = 28 percent
H/C ratio	--	1.0
Resistivity, Ω-cm	8.66×10^6	3.35×10^6
Optical band gap (eV)	0.382	0.343
Density, gm/cm^3	1.8	1.8
Index of refraction	2.0	2.46
Absorption coefficient/cm at 5000Å	5.15×10^4	4.26×10^4
Solar transmittance $t = \frac{\int Q(\lambda)T(\lambda)d(\lambda)}{\int Q(\lambda)d\lambda}$	0.519 Film = (1500 Å thick)	0.648 (1500 Å)
Adherence (Quartz)	$>5.5 \times 10^7$ N/m^2 >8000 psi	$>5.5 \times 10^7$ N/m^2 >8000 psi

Where: $Q(\lambda)$ = 6000°K black body
$T(\lambda)$ = transmittance at a given wavelength

TABLE II

Properties of Diamondlike Films Compared to Natural Diamond and Polycrystalline Diamond Films

Properties	Diamond	Polycrystalline Diamond Films	Diamond-Like Carbon Films
Microhardness (kg/mm^2)	10,000	8-10,000	3-5,000
Resistivity (ohm cm)	10^{13} - 10^{16}	10^{10} - 10^{15}	10^{7}
Thermal Conductivity (W/mK)	2,000	700	(7) Low
Refractive Index	2.4	2.3 - 2.4	2.4
Density (g/cm^3)	3.5	3.2 - 3.4	1.8
Friction Coefficient	0.1	--	<0.1 (at low humidity)
Chemical Resistance	High	High	High
Visible and Infrared Transparency	High	High	High
Visible and Infrared Specular Transparency	High	Low	High
Adherence	--	Low	High
Substrate Temperature During Deposition	--	>600° C	Room temperature or lower
Film Roughness	--	Rough	Smooth

TABLE III

Diamondlike Film Potential Applications Identified at LeRC

DLC Film Application	Desirable DLC Film Properties
1. Protective coating for sunglass lenses	Hardness, scratch resistance
2. Protective coating for eyeglass lenses	Hardness, scratch resistance, transmittance
3. Hermetic coating for eyewear	Hermeticity, hardness, scratch resistance, transmittance
4. Abrasion, moisture resistent coating for optical surfaces (visible and infrared)	Hermeticity, hardness, scratch resistance, transmittance
5. Magnetic recording head	Hermeticity, hardness, scratch resistance
6. Coating computer hard disk	Hermeticity, hardness, scratch resistance
7. Abrasion resistant coating for optical windows in bar code scanners	Hardness, scratch resistance
8. Biomedical applications	Biocompatibility, hermeticity
9. Chemically resistant protective coating	Hermeticity, hardness
10. Enhanced IR transmittance of Ge and Si infrared optics	IR transmittance, index of refraction, abrasion protection
11. Cutting blades	Smoothness, hardness, hermeticity
12. Abrasion resistant non-stick coating for cookware	Hardness, scratch resistance

TABLE IV

Focused Diamondlike Film Applications at Diamonex, Inc.

(1) Abrasion-resistant optical coatings

- Plastic sunglass lenses
- Plastic eyeglass lenses
- Other optical substrates such as glass

(2) Chemical/environmental protection ("hermetic sealing") of transparent substrates

- Quartz
- Glass
- Plastics

(3) Wear protection of non-optical substrates

- Magnetic disks
- Cutting surfaces
- Other wear parts

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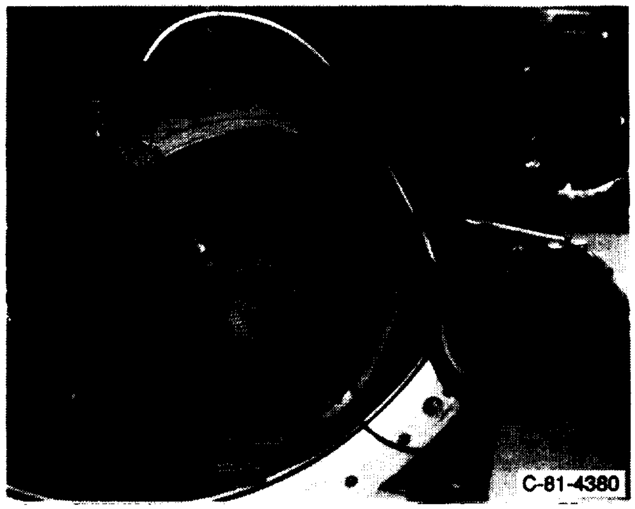

Figure 1.—Dual beam ion source for deposition of films with diamondlike properties.

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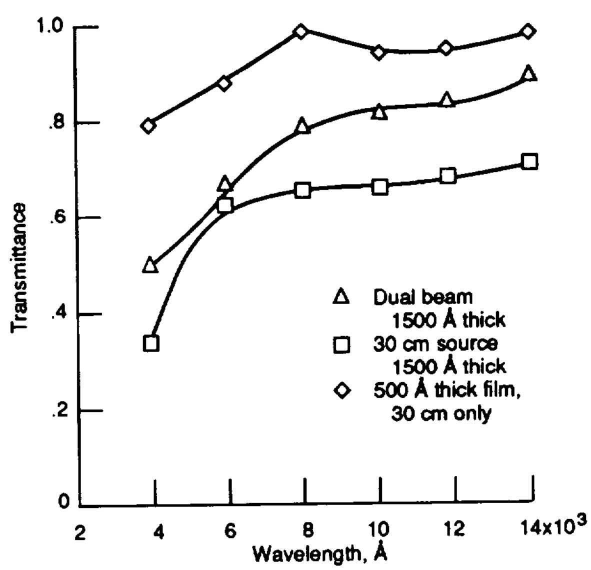

Figure 2.—Transmittance versus wavelength for DLC films using CH_4 in dual beam or single ion sources.

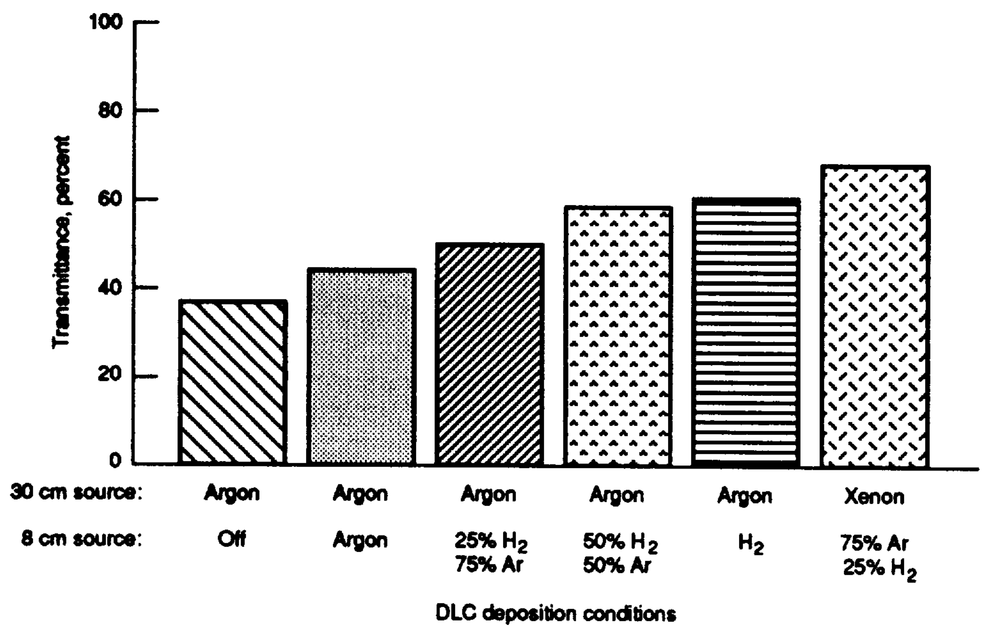

Figure 3.—Transmittance at 0.5 μm for 1000 Å thick DLC films deposited on quartz under various dual beam conditions.

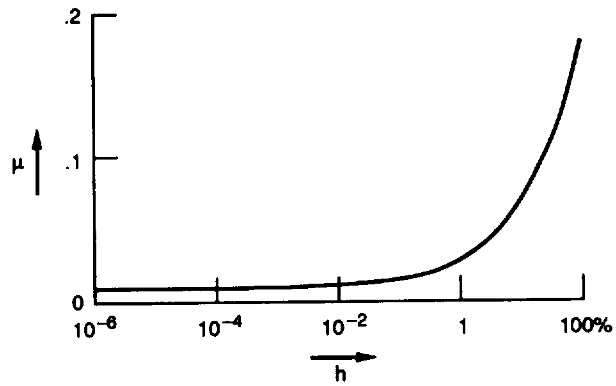

Figure 4.—Coefficient of friction μ for a diamondlike carbon film sliding on steel, as a function of the relative humidity h.

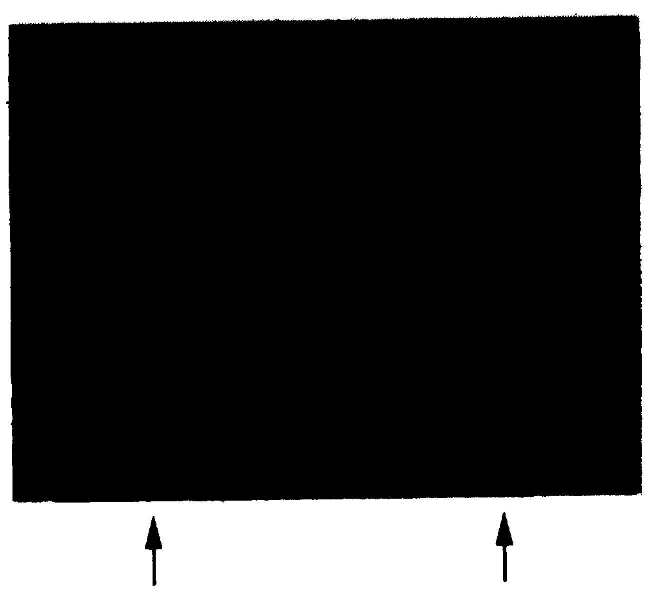

Figure 5.— Scratch test of DLC film using SiO_2 particles.